p-T-x Measurements for 1,1,1,2-Tetrafluoroethane (R134a) + N,N –dimethylacetamide (DMA), and N-methyl-2-pyrrolidone (NMP)

Raouf Zehioua, Christophe Coquelet, Abdeslam-Hassen Meniai

▶ **To cite this version:**

Raouf Zehioua, Christophe Coquelet, Abdeslam-Hassen Meniai. p-T-x Measurements for 1,1,1,2-Tetrafluoroethane (R134a) + N,N –dimethylacetamide (DMA), and N-methyl-2-pyrrolidone (NMP). Journal of Chemical and Engineering Data, 2016, 61 (2), pp.912-919. 10.1021/acs.jced.5b00747 . hal-01305709

HAL Id: hal-01305709

https://hal-mines-paristech.archives-ouvertes.fr/hal-01305709

Submitted on 21 Apr 2016

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

p-*T*-*x* Measurements for 1,1,1,2-Tetrafluoroethane (R134a) + N,N –dimethylacetamide (DMA), and N-methyl-2-pyrrolidone (NMP)

Raouf Zehioua[1*], Christophe Coquelet[2], Abdeslam-Hassen Meniai[1]

[1] *Laboratoire de l'Ingénierie des Procédés de l'Environnement (LIPE), Département de Génie Chimique, Université Constantine 3, Nouvelle ville Ali Mendjeli, Constantine 25000, Algérie*

[2] *Mines ParisTech, PSL Research University, CTP - Centre of Thermodynamic of Processes, 35 Rue Saint Honoré, 77305 Fontainebleau, France*

*Corresponding author: Dr. Raouf ZEHIOUA. E-mail: Zehiouaraouf@yahoo.ca

Abstract

The present study concerns *p-T-x* phase equilibria measurements involving two working fluid pairs (Refrigerant + Organic solvent) , namely 1,1,1,2-tetrafluoroethane (R134a) + N,N – dimethylacetamide (DMA) and , 1,1,1,2-tetrafluoroethane + N-methyl-2-pyrrolidone (NMP), using the static-analytic method at temperatures varying between 303 and 353 K. The experimentally measured data were successfully correlated using the Peng – Robinson equation of state (PR-EoS) in combination with Huron-Vidal mixing rule, and the non-random two liquid activity coefficient model (NRTL), contrarily to the predictive Soave-Redlich-Kwong (PSRK) group contribution equation of state which failed to reproduce accurately enough such data.

1. Introduction

Production of cold is one of the most important operations for a great number of human daily needs and activities and for various industrial fields. However due their nature, many refrigerant fluids may have a negative impact on the environment. Therefore one can measure the need for adequate working fluids which should be harmless towards the environment and efficient when used in compatible refrigeration machines. This has been a motivation factor for a great number of researchers aiming to find alternative refrigerant fluids as well as to develop new machine types mainly based on the absorption cycle.

In fact the performance of an absorption cycle based machines depends on several parameters of the refrigerant-absorbent pair[1], particularly the thermophysical and transport properties, the thermal stability and the phase equilibria taking place in different compartments.

Previous works carried out by the same present authors are reported in the literature and one can cite Zehioua et al[2,3]. who considered the modeling and experimental measurements of isothermal vapor-liquid equilibrium data for different binary systems namely 1, 1, 1, 2-Tetrafluoroethane (R134a) + Dimethylformamide (DMF) working fluids used for an Absorption Heat Transformer (AHT)[2] and R134a + 1-Methoxy-2-(2-methoxyethoxy) ethane (DMEDEG) and 1,2-bis(2-ethoxyethoxy) ethane (DMETrEG)[3]. Also Fatouh and Murthy[4] considered different working fluid pairs on the basis of *p-T-x-H* data, with R22 as the refrigerant and six different organic absorbents: [*N*,*N*-Dimethylformamide (DMF), *N*,*N*-Dimethylacetamide (DMA), *N*-methyl-2-pyrrolidone (NMP), Dimethylether Diethylene glycol (DMEDEG), Dimethylether tetra ethylene glycol (DMETEG), and

Dimethylether Triethylene glycol (DMETrEG)] still used in AHT. Similarly Borde et al.[5] considered the use of the refrigerant 1,1,1,2-tetrafluoroethane (R134a) as a substitute to CFC's in absorption heat pumps and refrigeration units and tested it in combination with different commercial absorbents such as Dimethylether tetra ethylene glycol (DMETEG), *N*-methyl ε-caprolactam (MCL), and Dimethylethylene urea (DMEU).

From a literature search, Jing et al.[6] measured the isothermal vapor−liquid equilibrium data of fluoroethane (R161) + N,N-dimethylacetamide (DMA), R161 + Nmethyl-2-pyrrolidone (NMP), and 1,1,1,2-tetrafluoroethane (R134a) + DMA were measured in a temperature range from (293.15 to 353.15) K.

Consequently the main purpose of the present work is the experimental study and modelling of phase equilibrium data involving another two working fluid pairs, namely R134a+DMA and R134a+NMP.

2. Experimental

2.1. Materials

The sources and the qualities of the used chemicals, as certified by the manufacturers, are presented in Table 1. Apart from a careful degassing of DMA and NMP, no further purification or pretreatment were performed.

2.2. Apparatus and Experimental Procedure

The measurements of *p*, *T*, *x* data of R134a + DMA and R134a + NMP binary systems were made using a "static-analytic" technique. This latter has already been described in details by Laugier and Richon[7]. Also a detailed description of the used apparatus and the adopted experimental procedure were given by Zehioua et al[2]. The equilibrium temperature was measured using two (Pt-100) platinum probes where a priori a 25 Ω reference platinum probe (Tinsley, France) was used to calibrate both temperature sensors. The standard uncertainty in the temperature measurements was estimated as 0.02 K. The equilibrium pressure was measured using a Druck pressure transducer (up to 4.0 MPa) which was calibrated by means of a dead weight balance (Desgranges and Huot model 5202S, France). The estimated relative standard uncertainty on pressure measurements was about 0.9%.

Liquid samples were analyzed by means of a gas chromatograph (Varian, CP – 3800), using a thermal conductivity detector (TCD) the calibration of which was made by introducing known pure component volumes with appropriate syringes. The resulting

accuracies concerning the mole number are 0.8% for R134, 1% for DMA and 1% for NMP, and the standard uncertainty on liquid mole fractions was estimated as about 0.007. The column used in the chromatograph was RTX-5-Amine (3 µm, 15 m × 0.53 mm ID).

3. Correlation

The correlation of the experimental measurements was obtained by the combination of the PR-EoS[8] with the Huron-Vidal mixing rule[9] and the NRTL model[10].

The critical properties of the considered components reported from the literature[11] are shown in Table 2.

The Huron-Vidal mixing rule is expressed as:

$$a = b\left(\sum_i x_i\left(\frac{a_i}{b_i}\right) + g^E_{p=\infty} \times C\right) \quad (1)$$

$$b = \sum_i x_i b_i \quad (2)$$

where a_i and b_i are the attractive parameter and the molar co-volume, respectively.

The excess Gibbs energy model based on NRTL is given by:

$$\frac{g^E(T, p, x_i)}{RT} = \sum_{i=1}^{n} x_i \frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{n} G_{ki} x_k} \quad (3)$$

Where n is the number of components in the system and

$$G_{ji} = \exp\left(-\alpha_{ji}\tau_{ji}\right) \quad (4)$$

$$\tau_{ji} = \left(g_{ji} - g_{ii}\right)/RT \quad (5)$$

α_{ij} and τ_{ij} are the non randomness and the adjustable binary parameters, respectively, with $\tau_{ii} = 0$, $\alpha_{ii} = 0$, $\alpha_{ij} = \alpha_{ji}$ and α_{ij} taken as equal to 0.3.

The binary NRTL parameters were fitted using the Simulis™ software package (from Prosim, Toulouse, France), for the minimization of the following objective function:

$$F = \frac{100}{N}\left[\sum_1^N \left(\frac{p_{i,\exp} - p_{i,cal}}{p_{i,\exp}}\right)^2\right] \quad (6)$$

where N is the number of experimental data points and p_{exp} and p_{cal} are the experimental and calculated pressures, respectively.

4. Results and discussion

The performance of the model used to correlate the experimental data was assessed by means of the following relative deviations, BIASP and AADP which are expressed as:

$$AADP = (100 / N)\sum_{i=1}^{N}\left|\left(p_{i,\exp} - p_{i,cal}\right)\Big/ p_{i,\exp}\right| \quad (7)$$

$$BIASP = (100 / N)\sum_{i=1}^{N}\left(\left(p_{i,\exp} - p_{i,cal}\right)\Big/ p_{i,\exp}\right) \quad (8)$$

Where N is the number of experimental measurements.

4.1. Pure component vapour pressure. In a previous work[2] experimental measurements of the vapour pressure of R134a were carried out at temperatures between 298 and 353 K. The obtained values were among the inputs to Simulis™ software surely to adjust the parameters of the Mathias - Copeman α function used in combination with the PR-EoS. The mean average absolute deviation between the experimental values and the calculated results using PR-EoS based model was about 0.25 %[2].

4.2. Vapour – liquid equilibrium for R134a + DMA and NMP binary mixtures. The experimentally measured and calculated isothermal VLE data for R134a + DMA and R134a + NMP binary systems at different temperatures are presented in Tables 3 and 4 and the plots in Figures 1 and 2. The NRTL parameters for Huron-Vidal mixing rules were adjusted to the obtained data at each temperature and are listed in Table 5. The relative deviations BIASP and the AADP values shown in Table 6, and represented in Figure 3 and 4, are encouraging indicating a reasonably good data prediction. The experimental VLE data of R134a + DMA was compared graphically with the values reported by Jing et al.[6] for the same system, as shown in Figure 1 where a reasonable agreement was noted. Using the present model the NRTL parameters adjusted to Jing et al.[6] data are listed in Table 5. The BIASP and AADP values are listed in Table 6.

4.3. Comparaison with the PSRK model. The PSRK equation of state is a combination of the Soave-Redlich-Kwong (SRK) equation of state and the UNIFAC group contribution model which is used to adapt the equation of state parameters for mixtures by a sort of a mixing rule which involves g^E, the molar excess Gibbs energy[12]. In the present work the PSRK equation

with Mathias-Copeman α function with parameters fitted to experimental vapor pressure data of pure components, was chosen to predict the VLE data for both considered binary systems.

The different functional groups involved in the molecular structure of each considered component as well as the corresponding interaction, volume and surface parameters are shown in Table 7[13].

Because of the important values of the relative and systematic deviations as illustrated by the BIASP and AADP values shown in Table 8, it is concluded that PSRK equation of state failed to predict the phase equilibrium data for the R134a + DMA, and + NMP binary systems.

5. Conclusions

The Isothermal solubility measurements were carried out, using a "static – analytic" method, for R134a + DMA and R134a + NMP mixtures at temperatures from 303 to 353 K and pressures up to 2.6 MPa with a standard uncertainty on liquid mole fractions estimated as about 0.007. The experimental data were successfully correlated by means of the Peng – Robinson EoS with Huron-Vidal mixing rules and the non-random two liquid (NRTL) activity coefficient model and the obtained results were in good agreement with the experimental values, contrarily to PSRK model which failed to predict accurately the data for both systems.

Acknowledgment

Mr Alain Valtz is gratefully acknowledged for its technical support.

Used symbols

a, parameter of the PR equation of state (energy parameter in $J.m^3.mol^{-2}$)

$a_{i,j}$, interaction parameters using in PSRK model (in K)

b, parameter of the PR equation of state (molar covolume parameter in m^3mol^{-1})

F, objective function

g^E, excess molar Gibbs energy in $J.mol^{-1}$

G_{ij}, local composition factor for the NRTL model (equation 4)

p, pressure in MPa

N, number of experimental measurements

q_k, relative van der Waals surface area of subgroup for PSRK equation of state

R, gas constant in $J.mol^{-1}.K^{-1}$

r_k, relative van der Waals volume of subgroup for PSRK equation of state

T, temperature in K

x, liquid mole fraction

y, vapor mole fraction

Greek letters

α_{ij}, nonrandomness NRTL model parameter

τ_{ij}, NRTL model binary interaction parameter

Superscript

E, excess property

Subscripts

c, critical property

cal, calculated property

exp, experimantal property

i,j,k, dummy index for component i, j and k

∞, infinite pressure references state

References

(1) Zheng, D. Ji, P.; Qi, J. Maximum excess Gibbs function of working pairs and absorption cycle performance. *Int. J. Refrig*. **2001**, *24*, 834-840.

(2) Zehioua, R.; Coquelet, C.; Meniai, A. H.; Richon, D. Isothermal Vapor-Liquid Equilibrium Data of 1,1,1,2-Tetrafluoroethane (R134a) + Dimethylformamide (DMF) Working Fluids for an absorption Heat Transformer. *J. Chem. Eng. Data.* **2010**, *55*, 985-988.

(3) Zehioua, R.; Coquelet, C.; Meniai, A. H.; Richon, D. *p-T-x* Measurements for Some Working Fluids for an Absorption Heat Transformer: 1,1,1,2-Tetrafluoroethane (R134a) + Dimethylether Diethylene Glycol (DMEDEG) and Dimethylether Triethylene Glycol (DMETrEG), *J. Chem. Eng. Data* **2010**, *55*, 2769–2775.

(4) Fatouh, M.; Murthy, S. S. Comparison of R22-absorbent pairs for vapor absorption heat transformers based on p-T-x-H data. *Heat Reco*V*ery Syst. CHP* **1993**, *13*, 33–48.

(5) Borde, I.; Jelinek, M.; Daltrophe, N. C. Absorption system based on refrigerant R134a. *Int. J. Refrig*. **1995**, *18*, 387–394.

(6) Jing, X.; Deng, R.; Zheng, D. Measurement and Correlation of Isothermal Vapor Liquid Equilibrium of Fluoroethane + N,N-Dimethylacetamide, Fluoroethane + N-Methyl-2-pyrrolidone, and 1,1,1,2-Tetrafluoroethane + N,N-Dimethylacetamide Systems. *J. Chem. Eng. Data*, **2013**, *58*, 3289-3296.

(7) Laugier, S.; Richon, D. New Apparatus to Perform Fast Determinations of Mixture Vapor-Liquid Equilibria up to 10 MPa and 423 K. *Rev. Sci. Instrum*. **1986**, *57*, 469 – 472.

(8) Peng, D.Y.; Robinson, D. B. A New Two Constant Equation of State. *Ind. Eng. Chem. Fundam*. **1976**, *15*, 59–64.

(9) Huron, M. J.; Vidal, J. New Mixing Rules in Simple Equations of State for Representing Vapour-Liquid Equilibria of Strongly non-ideal Mixtures. *Fluid Phase Equilib*. **1979**, *3*, 255-271

(10) Renon, H.; Prausnitz, J. M. Local Composition in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J*. **1968**, *14*, 135–144.

(11) *Dortmund Data Bank (DDB)*, Version 97, DDBST Software and Separation Technology GmbH, Oldenburg, Germany, 1997.

(12) Holderbaum, T.; Gmehling, J. PSRK: A Group Contribution Equation of State based on UNIFAC. *Fluid Phase Equilib*. **1991**, *70*, 251-265.

(13) Raal, J. D.; Mühlbauer, A. L. *Phase Equilibria : Measurement and Computation;* Taylor & Francis, Washington, 1999.

List of Tables

Table 1. Chemical samples used.

Chemical	CASRN	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
1,1,1,2-tetrafluoroethane (R134a)	811-97-2	ARKEMA	0.995	None	0.995	None
N,N – dimethylacetamide (DMA)	127-19-5	Aldrich	0.999	None	0.999	None
N-methyl-2-pyrrolidone (NMP)	872-50-4	Sigma -Aldrich	0.995	None	0.995	None

Table 2. Critical Parameters and acentric factors[11].

Chemical	p_C / MPa	T_C /K	ω
1,1,1,2-tetrafluoroethane (R134a)	4.064	374.25	0.32669
N,N – dimethylacetamide (DMA)	4.030	658.00	0.36351
N-methyl-2-pyrrolidone (NMP)	4.780	721.80	0.39503

Table 3. Experimental and Calculated VLE Data for R134a (1) + DMA (2) Binary Mixtures at Different Temperatures[a]

Experimental pressure p_{exp}/MPa	Calculated pressure p_{cal}/MPa	Experimental liquid mole fraction of R134a $x_{1,exp}$	Standard deviation repeatability δx	Calculated vapor mole fraction of DMA $(y_{2,cal}).10^2$	$(\Delta p/p_{exp})/\%$[b]
			***T*=303.3 K**		
0.2331	0.2291	0.3915	0.0009	0.111	1.7
0.2472	0.2438	0.4112	0.0027	0.101	1.4
0.2747	0.2725	0.4485	0.0029	0.086	0.8
0.3143	0.3147	0.5007	0.0068	0.068	-0.1
0.3509	0.3485	0.5406	0.0046	0.057	0.7
0.4083	0.4114	0.6112	0.0021	0.041	-0.8
0.4266	0.4273	0.6284	0.0038	0.038	-0.2
0.4642	0.4672	0.6711	0.0025	0.031	-0.7
0.4765	0.4852	0.6900	0.0030	0.028	-1.8
0.4915	0.5001	0.7056	0.0026	0.026	-1.8
0.5050	0.5113	0.7173	0.0028	0.024	-1.2
0.5290	0.5311	0.7379	0.0019	0.022	-0.4
0.5485	0.5512	0.7588	0.0019	0.019	-0.5
0.5936	0.6014	0.8112	0.0020	0.014	-1.3
0.6197	0.6326	0.8444	0.0022	0.011	-2.1
0.6366	0.6488	0.8619	0.0023	0.010	-1.9
0.6410	0.6527	0.8661	0.0011	0.009	-1.8
0.6664	0.6752	0.8909	0.0016	0.007	-1.3
0.6691	0.6779	0.8939	0.0014	0.007	-1.3
0.6819	0.6898	0.9072	0.0009	0.006	-1.2
0.6927	0.6986	0.9171	0.0011	0.006	-0.8
0.7020	0.7096	0.9296	0.0028	0.005	-1.1
0.7221	0.7227	0.9445	0.0015	0.004	-0.1
			***T*=313.15 K**		
0.4783	0.4664	0.5482	0.0015	0.081	2.5
0.5228	0.5162	0.5909	0.0019	0.067	1.3
0.5508	0.5451	0.6151	0.0025	0.060	1.0
0.5910	0.5903	0.6522	0.0036	0.051	0.1
0.6110	0.6123	0.6699	0.0030	0.047	-0.2
0.6413	0.6461	0.6970	0.0026	0.041	-0.7
0.6623	0.6690	0.7152	0.0029	0.038	-1.0
0.6826	0.6921	0.7335	0.0020	0.035	-1.4
0.6996	0.7081	0.7461	0.0020	0.032	-1.2
0.7365	0.7451	0.7754	0.0024	0.028	-1.2
0.7630	0.7707	0.7958	0.0015	0.025	-1.0
0.7865	0.7953	0.8155	0.0021	0.022	-1.1
0.7965	0.8061	0.8242	0.0012	0.021	-1.2

0.8082	0.8173	0.8333	0.0032	0.019	-1.1
0.8213	0.8297	0.8434	0.0014	0.018	-1.0
0.8316	0.8408	0.8526	0.0035	0.017	-1.1
0.8450	0.8556	0.8647	0.0022	0.015	-1.3
0.8748	0.8843	0.8888	0.0053	0.013	-1.1
0.9033	0.9125	0.9127	0.0022	0.010	-1.0
0.9204	0.9293	0.9272	0.0012	0.008	-1.0
			***T*=323.3 K**		
0.2158	0.2100	0.2124	0.0007	0.505	2.7
0.4420	0.4320	0.3974	0.0022	0.211	2.3
0.4772	0.4681	0.4247	0.0013	0.190	1.9
0.5655	0.5634	0.4939	0.0047	0.146	0.4
0.6291	0.6325	0.5420	0.0029	0.122	-0.5
0.6945	0.7080	0.5929	0.0040	0.101	-1.9
0.7361	0.7543	0.6236	0.0036	0.090	-2.5
0.7675	0.7918	0.6483	0.0027	0.082	-3.2
0.8000	0.8261	0.6706	0.0015	0.075	-3.3
0.9431	0.9730	0.7662	0.0028	0.050	-3.2
1.0222	1.0531	0.8193	0.0023	0.039	-3.0
1.0720	1.1006	0.8514	0.0006	0.032	-2.7
1.1102	1.1358	0.8756	0.0006	0.028	-2.3
1.1724	1.1934	0.9155	0.0006	0.020	-1.8
			***T*=338.3 K**		
0.3882	0.3804	0.2428	0.0022	0.631	2.0
0.4536	0.4529	0.2845	0.0006	0.521	0.2
0.4951	0.4914	0.3061	0.0010	0.476	0.8
0.5988	0.6014	0.3661	0.0017	0.377	-0.4
0.7112	0.7122	0.4242	0.0023	0.308	-0.1
0.7470	0.7648	0.4512	0.0024	0.282	-2.4
1.5447	1.5979	0.8597	0.0006	0.073	-3.4
1.5601	1.6112	0.8665	0.0010	0.070	-3.3
1.6042	1.6496	0.8861	0.0006	0.063	-2.8
1.6395	1.6861	0.9046	0.0023	0.056	-2.8
1.6794	1.7239	0.9235	0.0027	0.048	-2.6
			***T*=353.3 K**		
1.4043	1.3630	0.6025	0.0015	0.296	2.9
1.4894	1.4697	0.6369	0.0008	0.267	1.3
1.5654	1.5657	0.6673	0.0009	0.244	0.0
1.6698	1.6870	0.7051	0.0009	0.217	-1.0
1.7748	1.8159	0.7449	0.0007	0.192	-2.3
1.8434	1.8938	0.7689	0.0006	0.177	-2.7
2.1265	2.1942	0.8636	0.0005	0.125	-3.2
2.1982	2.2669	0.8873	0.0009	0.111	-3.1
2.2499	2.3150	0.9031	0.0015	0.102	-2.9
2.3137	2.3710	0.9215	0.0010	0.090	-2.5
2.3568	2.4054	0.9326	0.0022	0.083	-2.1

[a] Standard uncertainties (u) are : $u_r(p) \approx 0.9\%$, $u(T)= 0.02$ K, $u(x) \approx 0.007$. [b] Relative deviation of the pressure $(\Delta p/p_{exp})$: $(\Delta p/p_{exp})/\% = ((p_{cal} - p_{exp})/ p_{exp}).100$

Table 4. Experimental and Calculated VLE Data for R134a (1) + NMP (2) Binary Mixtures at Different Temperatures[a].

Experimental pressure p_{exp}/MPa	Calculated pressure p_{cal}/MPa	Experimental liquid mole fraction of R134a $x_{1,exp}$	Standard deviation repeatability δx	Calculated vapor mole fraction of NMP $(y_{2,cal}).10^2$	$(\Delta p/p_{exp})/\%$[b]
			T=303.3 K		
0.2926	0.2850	0.4386	0.0012	0.013	2.6
0.3451	0.3428	0.5076	0.0012	0.010	0.7
0.3828	0.3791	0.5492	0.0010	0.008	1.0
0.4140	0.4128	0.5868	0.0020	0.007	0.3
0.4253	0.4309	0.6068	0.0024	0.007	-1.3
0.4443	0.4415	0.6184	0.0012	0.006	0.6
0.4699	0.4723	0.6518	0.0013	0.005	-0.5
0.4861	0.4895	0.6705	0.0008	0.005	-0.7
0.4892	0.4956	0.6770	0.0019	0.005	-1.3
0.5091	0.5158	0.6988	0.0018	0.004	-1.3
0.5224	0.5241	0.7078	0.0017	0.004	-0.3
0.5595	0.5695	0.7573	0.0040	0.003	-1.8
0.5976	0.6129	0.8059	0.0038	0.003	-2.5
0.6267	0.6362	0.8329	0.0021	0.002	-1.5
0.6664	0.6780	0.8835	0.0029	0.002	-1.7
0.6677	0.6807	0.8868	0.0023	0.001	-1.9
0.6920	0.7013	0.9129	0.0022	0.001	-1.3
0.7729	0.7724	1	--	0.000	0.1
			T=313.15 K		
0.4478	0.4390	0.4898	0.0030	0.018	2.0
0.4951	0.4878	0.5327	0.0020	0.015	1.5
0.5311	0.5257	0.5653	0.0045	0.013	1.0
0.5795	0.5797	0.6109	0.0050	0.011	-0.1
0.6163	0.6219	0.6461	0.0050	0.010	-0.9
0.6491	0.6559	0.6744	0.0056	0.009	-1.1
0.7102	0.7253	0.7325	0.0063	0.007	-2.1
0.7389	0.7553	0.7581	0.0048	0.006	-2.2
0.7696	0.7909	0.7890	0.0039	0.005	-2.8
0.8260	0.8461	0.8388	0.0021	0.004	-2.4
0.8590	0.8780	0.8690	0.0007	0.003	-2.2
1.0188	1.0167	1	--	0.000	0.2
			T=323.15 K		
0.6960	0.6782	0.5487	0.0017	0.023	2.6
0.7522	0.7425	0.5914	0.0013	0.020	1.3
0.8568	0.8639	0.6713	0.0030	0.015	-0.8
0.8936	0.9086	0.7009	0.0042	0.014	-1.7

0.9448	0.9606	0.7360	0.0027	0.012	-1.7
1.0202	1.0433	0.7938	0.0018	0.010	-2.3
1.0697	1.0981	0.8340	0.0018	0.008	-2.6
1.1153	1.1383	0.8650	0.0015	0.007	-2.1
1.1533	1.1770	0.8957	0.0007	0.006	-2.1
1.3190	1.3203	1	--	0.000	-0.1
			***T*=338.3 K**		
1.0406	1.0194	0.5827	0.0033	0.042	2.0
1.0842	1.0559	0.5990	0.0061	0.040	2.6
1.1281	1.1158	0.6257	0.0051	0.037	1.1
1.1462	1.1324	0.6330	0.0039	0.036	1.2
1.1942	1.2027	0.6641	0.0054	0.033	-0.7
1.2304	1.2540	0.6868	0.0022	0.031	-1.9
1.2858	1.3150	0.7139	0.0031	0.028	-2.3
1.3245	1.3678	0.7376	0.0029	0.026	-3.3
1.3777	1.4228	0.7627	0.0015	0.024	-3.3
1.6696	1.7189	0.9120	0.0014	0.013	-3.0
1.8896	1.9049	1	--	0.000	-0.8
			***T*=353.45 K**		
1.1877	1.1585	0.4644	0.0034	0.112	2.5
1.3033	1.2842	0.5071	0.0038	0.102	1.5
1.3296	1.3141	0.5172	0.0025	0.099	1.2
1.3513	1.3582	0.5319	0.0020	0.096	-0.5
1.4049	1.4271	0.5549	0.0022	0.092	-1.6
1.4744	1.5331	0.5902	0.0033	0.085	-4.0
2.2973	2.4009	0.9121	0.0010	0.042	-4.5
2.6059	2.6661	1	--	0.000	-2.3

a Standard uncertainties (u) are : $u_r(p) \approx 0.9\%$, $u(T)= 0.02$ K, $u(x) \approx 0.007$. **b** Relative deviation of the pressure $(\Delta p/p_{exp})$: $(\Delta p/p_{exp})/\% = ((p_{cal} - p_{exp})/ p_{exp}).100$

Table 5. NRTL Adjusted Parameters for Huron-Vidal Mixing Rules.

R134a (1) + DMA (2)						R134a (1) + NMP (2)		
Present work			Jing et al.[6]					
T/K	τ_{12}/J.mol^{-1}	τ_{21}/J.mol^{-1}	*T*/K	τ_{12}/J.mol^{-1}	τ_{21}/J.mol^{-1}	*T*/K	τ_{12}/J.mol^{-1}	τ_{21}/J.mol^{-1}
303.30	848	-1017	**293.15**	2779	-993	**303.30**	803	-995
313.15	838	-1027	**303.15**	1965	-1021	**313.15**	803	-990
323.30	787	-941	**313.15**	1459	-1000	**323.15**	703	-914
338.30	760	-866	**323.15**	526	-703	**338.30**	917	-1066
353.30	818	-1045	**333.15**	659	-795	**353.45**	846	-946
			343.15	772	-927			
			353.15	806	-981			

Table 6. Relative Deviations BIASP and AADP Using PR EoS with Huron-Vidal Mixing Rules and NRTL Activity Coefficient Model.

R134a (1) + DMA (2)								R134a (1) + NMP (2)			
Present work				Jing et al.[6]							
T/K	N^a	AADP/%	BIASP/%	*T*/K	N^a	AADP/%	BIASP/%	*T*/K	N^a	AADP/%	BIASP/%
303.30	23	1.1	-0.7	**293.15**	08	9.3	3.8	**303.30**	18	1.2	-0.6
313.15	20	1.1	-0.6	**303.15**	08	6.7	3.6	**313.15**	12	1.5	-0.8
323.30	14	2.3	-1.2	**313.15**	09	6.5	4.0	**323.15**	10	1.7	-0.9
338.30	11	1.9	-1.4	**323.15**	09	5.1	3.7	**338.30**	11	2.0	-0.8
353.30	11	2.2	-1.4	**333.15**	09	7.2	-0.6	**353.45**	08	2.2	-1.0
				343.15	11	6.5	0.8				
				353.15	10	5.1	3.3				

[a] *N* is the number of experimental measurements.

Table 7. PSRK Parameters; the van der Waals Properties and the Interaction Parameters[13].

Group	Sub group	R134a	DMA	NMP	r_k	q_k	a_{ij}/ K		
							40	1	39
40	CF_3	1			1.4060	1.3800	0.000	147.30	55.80
	CF	1			0.6150	0.4600			
1	CH_3		1	1	0.9011	0.8480	-2.859	0.000	485.30
	CH_2			1	0.6744	0.5400			
39	$HCON(CH_2)_2$			1	2.6322	2.120	-5.579	-31.95	0.000
	DMF : $((HCON(CH_3)_2)$		1		3.0856	2.736			

Table 8. Relative Deviations BIASP and AADP with respect to the PSRK Model

R134a (1) + DMA (2)			R134a (1) + NMP (2)		
***T*/K**	**AADP/%**	**BIASP/%**	***T*/K**	**AADP/%**	**BIASP/%**
303.30	18	-18	**303.30**	22	-22
313.15	15	-15	**313.15**	23	-23
323.30	21	-21	**323.15**	15	-15
338.30	18	-18	**338.30**	14	-14
353.30	16	-16	**353.45**	15	-15

List of Figures

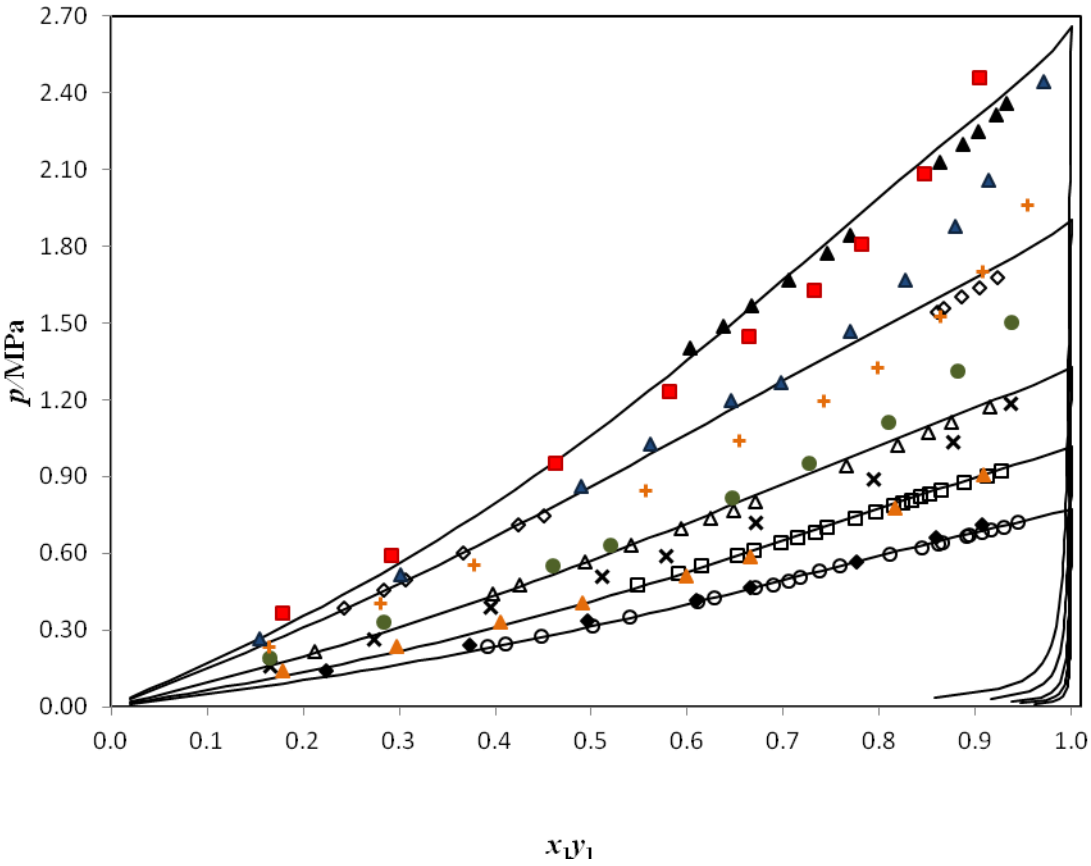


Figure 1. Vapor – Liquid equilibrium isotherms for R134a (1) + DMA(2) binary system : ○, 303 K; □, 313 K; Δ, 323 K; ◊, 338 K; ▲, 353 K; Literature data[6]: ♦, 293.15 K; ▲, 303.15 K; ×, 313.15 K; ●, 323.15 K; +, 333.15 K; ▲, 343.15 K; ■, 353.15 K; solid lines, calculated results using PR-NRTL using the Huron-Vidal mixing rules.

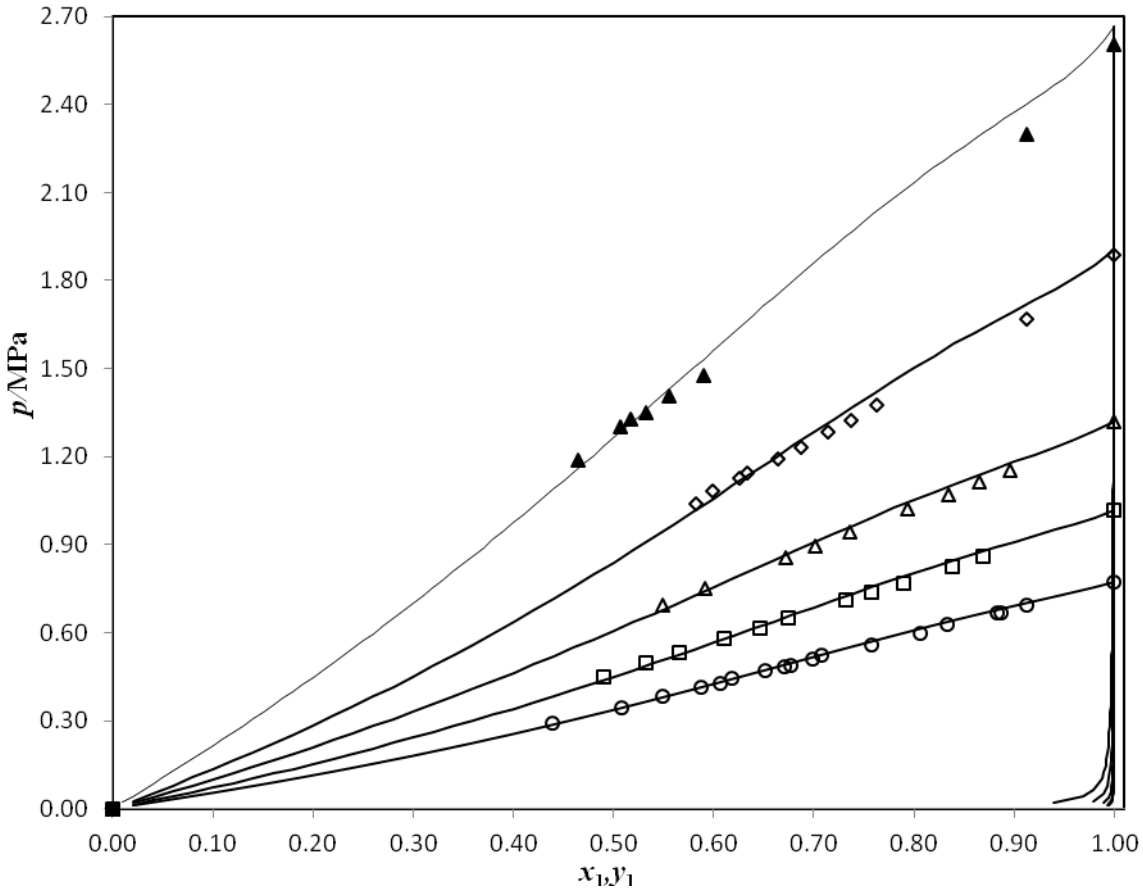
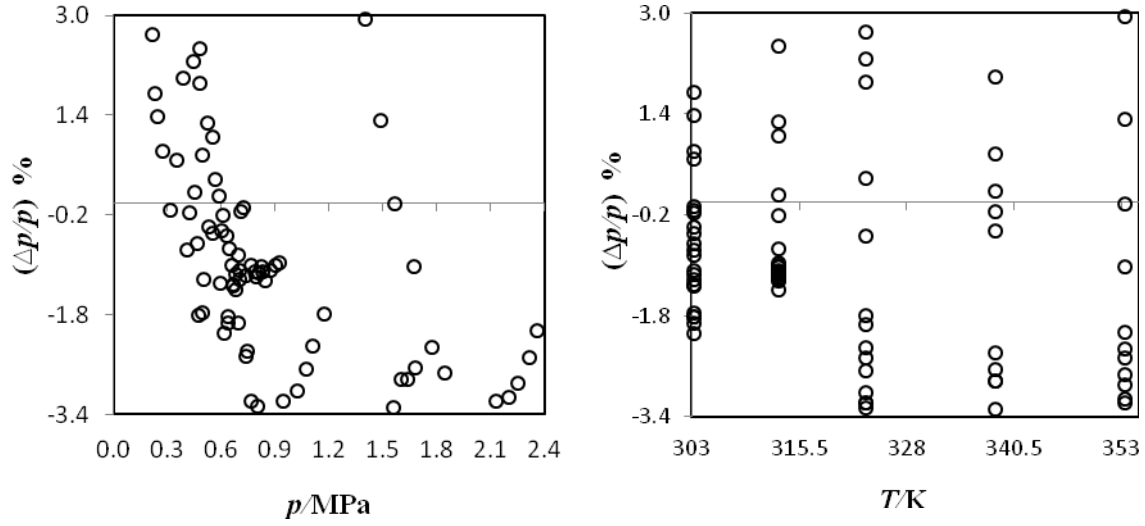
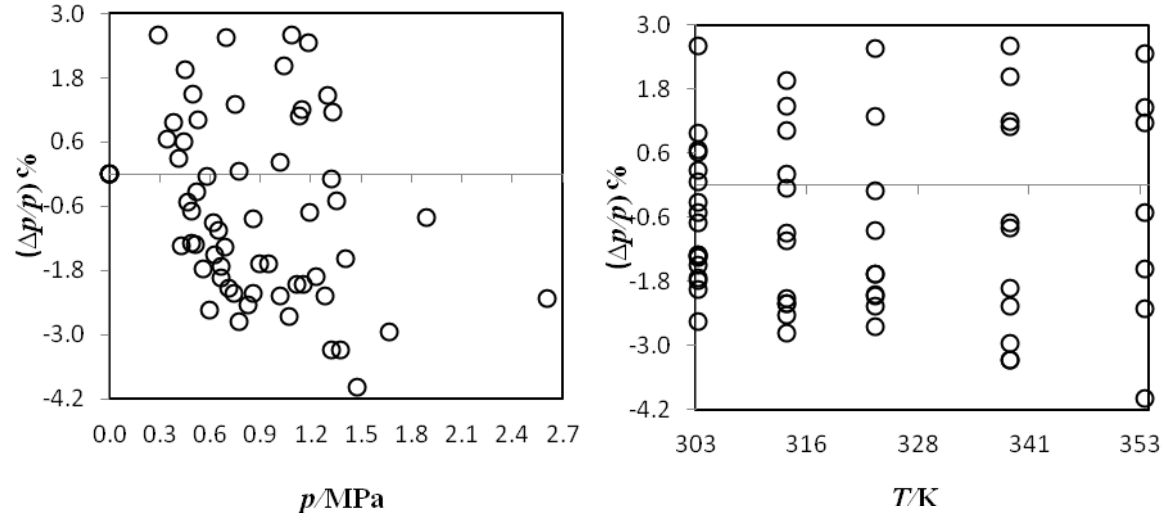


Figure 2. Vapor – Liquid equilibrium isotherms for R134a (1) + NMP (2) binary system: ○, 303 K; □, 313 K; Δ, 323 K; ◊, 338 K; ▲, 353 K; solid lines, calculated results using PR-NRTL using the Huron-Vidal mixing rules.



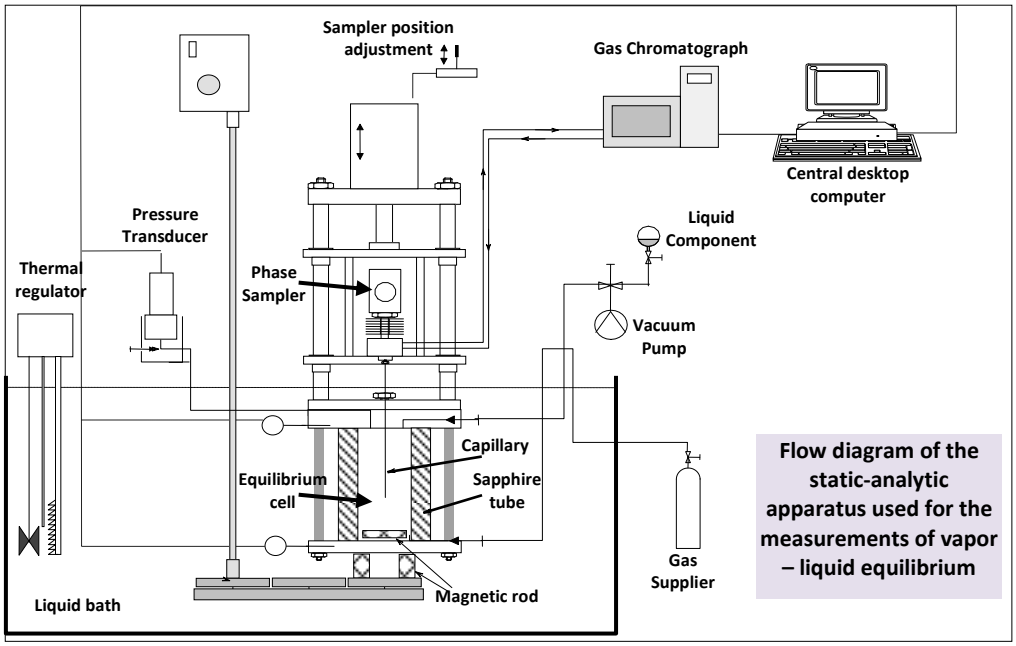
a b

Figure 3. Relative Pressure deviations of the measured and the calculated data, using PR-NRTL using the Huron-Vidal mixing rules, for R134a (1) + DMA (2) system : (a) as a function of Pressures; (b) as a function of Temperatures.



a b

Figure 4. Relative Pressure deviations of the measured and the calculated data, using PR-NRTL using the Huron-Vidal mixing rules, for R134a (1) + NMP (2) system: (a) as a function of Pressures; (b) as a function of Temperatures.



Flow diagram of the static-analytic apparatus used for the measurements of vapor – liquid equilibrium